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Dr. Judah Goldwasser

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SOME APPROXIMATE KOHN-SHAM MOLECULAR ENERGY FORMULAS

by

Peter Politzer and Fakher Abu-Awwad

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Department of Chemistry  
University of New Orleans  
New Orleans, LA 70148

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# Some Approximate Kohn-Sham Molecular Energy Formulas

Peter Politzer and Fakhre Abu-Awwad

Department of Chemistry  
University of New Orleans  
New Orleans, Louisiana 70148

## Abstract

Density functional calculations have been carried out for twelve molecules by several different Kohn-Sham procedures in order to test the effectiveness of two approximate molecular energy formulas that have been applied earlier in the context of Hartree-Fock theory. The equation  $E_{\text{molecular}} = \frac{3}{7} (V_{\text{ne}} + 2V_{\text{nn}})$ , in which  $V_{\text{ne}}$  and  $V_{\text{nn}}$  are the nuclear-electronic attraction and nuclear repulsion, reproduces Kohn-Sham energies with an average deviation of less than 0.70%.  $E_{\text{molecular}} = \alpha \sum n_i \epsilon_i$ , where  $n_i$  and  $\epsilon_i$  are the molecular orbital occupancies and energies, gives an average deviation of 1.6%, with  $\alpha$  determined empirically for each functional combination. The relationship  $3E_{\text{molecule}} = 1.14 \sum n_i \epsilon_i + 2V_{\text{nn}} + V_{\text{ne}}$ , an analogue of an exact Hartree-Fock expression, predicts Becke-3 Kohn-Sham molecular energies to within an average 0.23% of the actual values.

## 1. Background

The Hellmann-Feynman theorem can be written in the form [1-3],

$$\left( \frac{\partial E}{\partial Z_A} \right)_N = V_{0,A} \quad (1)$$

in which  $E$  is the total energy of an  $N$ -electron atom or molecule and  $V_{0,A}$  is the electrostatic potential at nucleus  $A$  due to the electrons and other nuclei:

$$V_{0,A} = \sum_{B \neq A} \frac{Z_B}{|\mathbf{R}_B - \mathbf{R}_A|} - \int \frac{\rho(\mathbf{r}) d\mathbf{r}}{|\mathbf{r} - \mathbf{R}_A|} \quad (2)$$

$Z_B$  is the charge on nucleus  $B$ , located at  $\mathbf{R}_B$ , and  $\rho(\mathbf{r})$  is the electronic density.

Eq. (1) suggests that it should be possible to express energies rigorously in terms of electrostatic potentials at nuclei, and such formulas have indeed been derived [4]:

$$E_{\text{atom}} = \frac{1}{2} Z V_0 - \frac{1}{2} \int_0^Z \left[ Z' \left( \frac{\partial V_0}{\partial Z'} \right) - V_0 \right]_{\text{N}} dZ' \quad (3)$$

$$E_{\text{molecule}} = \frac{1}{2} \sum_A Z_A V_{0,A} - \frac{1}{2} \sum_A \int_0^{Z_A} \left[ Z'_A \left( \frac{\partial V_{0,A}}{\partial Z'_A} \right) - V_{0,A} \right]_{\text{N}} dZ'_A \quad (4)$$

The molecular formula, eq. (4), has the notable feature that it is simply a summation over atomic contributions, with no explicitly interaction or mixing terms.

The quantity  $ZV_0$  in eq. (3) is the nuclear-electronic attraction energy,  $V_{\text{ne}}$ , while  $\sum_A Z_A V_{0,A}$  in eq. (4) equals  $V_{\text{ne}} + 2V_{\text{nn}}$ ,  $V_{\text{nn}}$  being the nuclear repulsion. It follows from the virial theorem that the electronic repulsion energies are included in the integral terms in eqs. (3) and (4). Thus, these two-electron quantities can be evaluated rigorously from the one-electron properties  $V_0$  and  $V_{0,A}$ .

Within the framework of the Thomas-Fermi model [5-7], which is an early and approximate version of density functional theory,

$$E_{\text{atom}} = \frac{3}{7} Z V_0 = \frac{3}{7} V_{\text{ne}} \quad (5)$$

Eq. (5) can be regarded as a simplified form of eq. (3). Using Hartree-Fock values for  $V_0$ , eq. (5) reproduces the Hartree-Fock atomic energies to within an average of about 2% [4,8]. In the spirit of eq. (4), the extension of eq. (5) to molecules by just summing over the atomic contributions was tested [9]:

$$E_{\text{molecule}} = \frac{3}{7} \sum_A Z_A V_{0,A} = \frac{3}{7} (V_{\text{ne}} + 2V_{\text{nn}}) \quad (6)$$

The average error obtained with eq. (6), relative to the Hartree-Fock energy, is in the neighborhood of 1% [9].

In Hartree-Fock theory, the energy of a molecule can be expressed exactly by [10],

$$E_{\text{molecule}} = \sum_i n_i \epsilon_i + V_{\text{nn}} - V_{\text{ee}} \quad (7)$$

where the  $n_i$  and  $\epsilon_i$  are the occupancies and energies of the molecular orbitals. Eq. (7) can be combined with the virial theorem to give,

$$3E_{\text{molecule}} = \sum_i n_i \epsilon_i + V_{\text{ne}} + 2V_{\text{nn}} \quad (8)$$

If eq. (6) is inserted into eq. (8), the result, as shown initially by Ruedenberg [11], is,

$$E_{\text{molecule}} = \frac{3}{2} \sum_i n_i \epsilon_i \quad (9)$$

Eq. (9) would be exact within the framework of Hartree-Fock theory if eq. (6) were rigorously correct. In practice, Ruedenberg found eq. (9) to be satisfied to within 2 - 4% [11].

While the accuracies obtained with eqs. (6) and (9) are clearly not sufficient to permit the direct calculation of reaction energetics, these relationships have aroused considerable interest, on both conceptual and applied levels [12-46]. Accordingly, we have now examined the validity of eq. (6) in the context of Kohn-Sham density functional methodology. Since eq. (7) is no longer applicable, neither is the derivation of eq. (9); however, we have investigated empirically the possibility of replacing the factor  $\frac{3}{2}$  in eq. (9) by some other constant.

## 2. Procedure

We have carried out Kohn-Sham calculations for 12 molecules of various types, using five different combinations of functionals and basis sets. The former include the Becke (B) [47], the Becke-3 (B3) [48], the Perdew-86 (P86) [49], the Lee/Yang/Parr (LYP) [50] and the Perdew/Wang-91 (PW91) [51]. The basis sets were the 6-31+G\*\* and 6-311++G(3df,3pd). For purposes of comparison, we also include Hartree-Fock treatments at two levels, HF/3-21G and HF/6-31+G\*\*. All geometries were optimized by the respective procedures, using the Gaussian 94 code [52]. Finally, in order to verify that our findings extend to larger molecules as well, HF/6-31+G\*\* and B3P86/6-31+G\*\* calculations were carried out for benzene, aniline and nitrobenzene.

## 3. Results

Table 1 lists the key computed energy quantities obtained for twelve molecules by seven different procedures. The extent to which eq. (6) is obeyed in each instance is shown in Table 2, while the ratios  $E_{\text{molecule}} / \sum_i n_i \epsilon_i$ , which are relevant to eq. (9), are in Table 3. The results for benzene, aniline and nitrobenzene are given in Table 4.

It is seen in Table 1 that eq. (6) generally overestimates the magnitudes of the Hartree-Fock total energies, whereas the Kohn-Sham are overestimated and underestimated to roughly the same extent. However Table 2 shows that the average deviations are less than 1% of the correct values. It is notable that they are little affected by increasing the basis set or by changing the functional combination.

If eq. (9) were satisfied exactly by the Hartree-Fock data, the ratio  $E_{\text{molecule}}/\sum n_i \epsilon_i$  would be 1.500. Table 3 shows that it actually ranges between 1.48 and 1.64; the average is 1.55, as was pointed out earlier by Ruedenberg [11]. For the Kohn-Sham results, it can be anticipated that this ratio will be greater than for the Hartree-Fock, since the Kohn-Sham orbital energies are known to be considerably smaller in magnitude [53]. Indeed the BLYP values of  $E_{\text{molecule}}/\sum n_i \epsilon_i$  are between 1.75 and 1.85; for the B3 functional combinations they are somewhat lower, between 1.69 and 1.80, perhaps reflecting the partial inclusion of the Hartree-Fock exchange energy [48,52].

Table 4 confirms that benzene, aniline and nitrobenzene fit in well with the smaller molecules, in terms of both eq. (6) and the  $E_{\text{molecule}}/\sum n_i \epsilon_i$  ratio. The degree to which the Hartree-Fock data satisfy eqs. (6) and (9) is particularly striking.

#### 4. Discussion

As was pointed out earlier, if eq. (6) were satisfied exactly in Hartree-Fock theory, then eq. (9) would be as well. For example, the HF/3-21G and HF/6-31+G\*\* results for diazirine deviate from eq. (6) by only 0.13% and 0.19% (Table 2), and the ratios  $E_{\text{molecule}}/\sum n_i \epsilon_i$  are correspondingly very close to the theoretical 1.500, at 1.512 and 1.514 (Table 3). In fact the Hartree-Fock data show excellent linear correlations between the percent deviation from eq. (6) and the ratio  $E_{\text{molecule}}/\sum n_i \epsilon_i$  (Figure 1); as the deviation approaches zero, the ratio approaches 1.500. The least squares plots for the 3-21G and 6-31+G\*\* basis sets can almost be superposed, and they predict 1.505 and 1.504, respectively, as the values for the ratio at zero deviation.

We have shown empirically that an equation of the form,

$$E_{\text{molecule}} = \alpha \sum_i n_i \epsilon_i \quad (10)$$

is a reasonable approximation in Kohn-Sham theory, accurate to within about 1.6%. At the BLYP level,  $\alpha$  is about 1.79, and for the B3 functional combinations it is about 1.73 (Table 3). (The four B3 values for each molecule are nearly the same.) However in the absence of an equivalent of eq. (7) or eq. (8), there appears to be no reason to anticipate a correlation between the deviation from eq. (6) and the ratio  $E_{\text{molecule}}/\sum n_i \epsilon_i$ . It is therefore particularly interesting that such

correlations do exist (Figures 2 and 3). The five plots are quite similar in appearance, although the BLYP is somewhat displaced from the others in the vertical direction.

The existence of these relationships suggests that attention be focused upon the value of  $E_{\text{molecule}} / \sum n_i \epsilon_i$  that corresponds to zero deviation from eq. (6). For the B3 results, this is about 1.717; for the BLYP, it is 1.772. Since eq. (6) is satisfied at these points, the derivation of eq. (9) can be reversed, using the appropriate factor instead of  $3/2$ , to arrive at analogues of eqs. (7) and (8). For example, for the B3 functional combinations,

$$E_{\text{molecule}} = 1.717 \sum_i n_i \epsilon_i = \frac{3}{2} (1.145) \sum_i n_i \epsilon_i$$

$$\frac{2}{3} E_{\text{molecule}} = 1.145 \sum_i n_i \epsilon_i$$

$$\frac{2}{3} E_{\text{molecule}} + \frac{7}{3} E_{\text{molecule}} = 1.145 \sum_i n_i \epsilon_i + \frac{7}{3} E_{\text{molecule}} = 1.145 \sum_i n_i \epsilon_i + 2V_{\text{nn}} + V_{\text{ne}}$$

$$3E_{\text{molecule}} = 1.145 \sum_i n_i \epsilon_i + 2V_{\text{nn}} + V_{\text{ne}} \quad (11)$$

$$E_{\text{molecule}} = 1.145 \sum_i n_i \epsilon_i + V_{\text{nn}} - V_{\text{ee}} \quad (12)$$

Eqs. (11) and (12) can be regarded as approximate Kohn-Sham analogues of the exact Hartree-Fock eqs. (8) and (7). Using the data in Tables 1 and 4, eq. (11) reproduces the respective B3 total energies to a notable degree of accuracy, the average absolute deviation being only 0.20%.

## 5. Summary

The key points to come out of this work are the following:

- (1) Eq. (6) predicts Kohn-Sham molecular energies to within an average 0.70% of the actual values.
- (2) Eq. (10), with appropriate values of  $\alpha$ , predicts Kohn-Sham molecular energies to within an average 1.6%.
- (3) Eqs. (11) and (12) are approximate B3 Kohn-Sham analogues of the exact Hartree-Fock eqs. (8) and (7). Eq. (11) predicts B3 Kohn-Sham molecular energies to within an average 0.20%.

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## Figure Captions

Figure 1. Relationship between  $E_{\text{mol}}/\sum n_i \epsilon_i$  and percent deviation from eq. (6), for HF/6-31+G\*\* results. The correlation coefficient is 0.9996.

Figure 2. Relationship between  $E_{\text{mol}}/\sum n_i \epsilon_i$  and percent deviation from eq. (6), for BLYP/6-31+G\*\* results. The correlation coefficient is 0.979.

Figure 3. Relationship between  $E_{\text{mol}}/\sum n_i \epsilon_i$  and percent deviation from eq. (6), for B3P86/6-311++G(3df,3pd) results. The correlation coefficient is 0.969.

Table 1. Energy quantities (in hartrees) computed by various Hartree-Fock and Kohn-Sham procedures.

Molecule	Method	$\sum n_i \epsilon_i$	$V_{ne}$	$V_{nn}$	$E_{mol}$	$\frac{3}{7}(V_{ne} + 2V_{nn})$	$E_{mol} / \sum n_i \epsilon_i$
CO <sub>2</sub>	HF/3-21G	-119.14656	-557.21501	58.61176	-186.56126	-188.56778	1.566
	HF/6-31+G**	-119.88572	-560.97467	59.24030	-187.63879	-189.64032	1.565
	BLYP/6-31+G**	-104.20517	-557.20143	57.24861	-188.57493	-189.73038	1.810
	B3PW91/6-31+G**	-108.21846	-558.76543	58.01606	-188.51416	-189.74285	1.742
	B3LYP/6-31+G**	-108.28888	-558.56526	57.92479	-188.59039	-189.73529	1.742
	B3P86/6-31+G**	-108.70146	-558.83696	58.04844	-188.97159	-189.74575	1.738
	B3P86/6-311++G(3df,3pd)	-108.48572	-561.24433	58.54051	-189.04019	-190.35570	1.743
H <sub>2</sub> O	HF/3-21G	-46.88150	-197.91022	9.09750	-75.58596	-77.02081	1.612
	HF/6-31+G**	-47.52970	-198.98339	9.32659	-76.03123	-77.28438	1.600
	BLYP/6-31+G**	-41.63718	-198.26922	9.01984	-76.41614	-77.24123	1.835
	B3PW91/6-31+G**	-42.87088	-198.58446	9.14236	-76.40460	-77.27132	1.782
	B3LYP/6-31+G**	-42.89938	-198.53074	9.11835	-76.43405	-77.26887	1.782
	B3P86/6-31+G**	-43.08370	-198.59087	9.14347	-76.61055	-77.27311	1.778
	B3P86/6-311++G(3df,3pd)	-43.02810	-199.21893	9.17517	-76.64039	-77.51511	1.781
	HF/3-21G	-97.21484	-470.19589	63.43751	-146.94779	-147.13752	1.512
	HF/6-31+G**	-97.64528	-476.57497	65.47801	-147.84286	-148.12241	1.514
	BLYP/6-31+G**	-84.51436	-472.25913	63.18057	-148.69499	-148.24200	1.759
	B3PW91/6-31+G**	-87.31958	-474.35858	64.22646	-148.67137	-148.24528	1.703
	B3LYP/6-31+G**	-87.36300	-473.93568	64.02022	-148.72958	-148.24082	1.702
	B3P86/6-31+G**	-87.78808	-474.44619	64.26173	-149.11961	-148.25260	1.699
	B3P86/6-311++G(3df,3pd)	-87.64732	-476.06250	64.56870	-149.16232	-148.68219	1.702
C <sub>2</sub> H <sub>2</sub>	HF/3-21G	-51.32042	-227.76891	25.08368	-76.39596	-76.11495	1.489
	HF/6-31+G**	-51.60650	-228.78952	25.01758	-76.82722	-76.60901	1.489
	BLYP/6-31+G**	-44.05488	-227.74856	24.48827	-77.30421	-76.61658	1.755
	B3PW91/6-31+G**	-45.63938	-228.18429	24.66884	-77.30028	-76.64855	1.694
	B3LYP/6-31+G**	-45.68742	-228.16747	24.67398	-77.33714	-76.63693	1.693
	B3P86/6-31+G**	-45.92880	-228.23343	24.68541	-77.57956	-76.65540	1.689
	B3P86/6-311++G(3df,3pd)	-45.86882	-229.13318	24.87513	-77.60347	-76.87839	1.692

(continued)

Table 1. Energy quantities (in hartrees) computed by various Hartree-Fock and Kohn-Sham procedures (continued).

Molecule	Method	$\sum n_i \epsilon_i$	$V_{ne}$	$V_{nn}$	$E_{mol}$	$\frac{3}{7}(V_{ne} + 2V_{nn})$	$E_{mol} / \sum n_i \epsilon_i$
N <sub>2</sub>	HF/3-21G	-70.70226	-301.87823	23.94612	-108.30095	-108.85114	1.532
	HF/6-31+G**	-71.09528	-303.46190	24.04848	-108.94702	-109.44212	1.532
	BLYP/6-31+G**	-62.06626	-301.93565	23.19942	-109.51768	-109.51578	1.765
	B3PW91/6-31+G**	-63.95556	-302.53453	23.48633	-109.48157	-109.52652	1.712
	B3LYP/6-31+G**	-64.00520	-302.47040	23.46316	-109.52978	-109.51889	1.711
	B3P86/6-31+G**	-64.26038	-302.55521	23.49515	-109.76926	-109.52782	1.708
	B3P86/6-31++G(3df,3pd)	-64.12424	-304.04527	23.77937	-109.80579	-109.92280	1.712
$\begin{array}{c} \text{CH} \\ \diagup \quad \diagdown \\ \text{H}_2\text{C}=\text{C} \\ \diagdown \quad \diagup \\ \text{CH} \end{array}$	HF/3-21G	-77.80246	-395.39628	63.96494	-115.16200	-114.62846	1.480
	HF/6-31+G**	-78.11118	-398.00208	64.35838	-115.83401	-115.40799	1.483
	BLYP/6-31+G**	-66.51502	-395.52316	63.12959	-116.57038	-115.39885	1.753
	B3PW91/6-31+G**	-68.98064	-396.94647	63.77973	-116.58642	-115.45158	1.690
	B3LYP/6-31+G**	-69.03684	-396.66778	63.66149	-116.63147	-115.43349	1.689
	B3P86/6-31+G**	-69.43638	-397.06517	63.82665	-117.02582	-115.46223	1.685
	B3P86/6-31++G(3df,3pd)	-69.35532	-398.39164	64.13144	-117.05701	-115.76947	1.688
H <sub>2</sub> C=C=O	HF/3-21G	-98.49238	-471.51278	58.90615	-150.87653	-151.58592	1.532
	HF/6-31+G**	-99.07112	-474.08699	59.14038	-151.73411	-152.48838	1.532
	BLYP/6-31+G**	-85.85062	-471.40383	57.71617	-152.57461	-152.55921	1.777
	B3PW91/6-31+G**	-88.63390	-472.68035	58.32299	-152.54746	-152.58616	1.721
	B3LYP/6-31+G**	-88.69890	-472.50177	58.24700	-152.61090	-152.57476	1.721
	B3P86/6-31+G**	-89.10086	-472.77709	58.36190	-152.99597	-152.59427	1.717
	B3P86/6-31++G(3df,3pd)	-88.96686	-474.74023	58.81312	-153.04672	-153.04885	1.720
N <sub>2</sub> O	HF/3-21G	-117.84926	-549.07581	59.78678	-182.60563	-184.07239	1.549
	HF/6-31+G**	-118.78702	-555.52492	61.90669	-183.68528	-185.01923	1.546
	BLYP/6-31+G**	-104.05520	-551.33643	59.56057	-184.66240	-185.23512	1.775
	B3PW91/6-31+G**	-107.18794	-553.38216	60.61426	-184.59574	-185.20870	1.722
	B3LYP/6-31+G**	-107.23626	-552.96702	60.40855	-184.66830	-185.20711	1.722
	B3P86/6-31+G**	-107.67188	-553.42734	60.63537	-185.05242	-185.20997	1.719
	B3P86/6-31++G(3df,3pd)	-107.48148	-556.04082	61.24827	-185.11643	-185.80469	1.722

(continued)

Table 1. Energy quantities (in hartrees) computed by various Hartree-Fock and Kohn-Sham procedures (continued).

Molecule	Method	$\sum n_i \epsilon_i$	$V_{ne}$	$V_{nn}$	$E_{mol}$	$\frac{3}{7}(V_{ne} + 2V_{nn})$	$E_{mol} / \sum n_i \epsilon_i$
FCN	HF/3-21G	-120.55844	-561.77109	55.54282	-190.63774	-193.15091	1.581
	HF/6-31+G**	-121.42870	-566.03098	56.41500	-191.70393	-194.22899	1.579
	BLYP/6-31+G**	-106.62816	-562.35979	54.52259	-192.62499	-194.27769	1.807
	B3PW91/6-31+G**	-109.74250	-564.01307	55.33000	-192.56512	-194.29417	1.755
	B3LYP/6-31+G**	-109.80218	-563.77315	55.21352	-192.64309	-194.29119	1.754
	B3P86/6-31+G**	-110.22558	-564.11268	55.37604	-193.02208	-194.29740	1.751
	B3P86/6-31++G(3df,2pd)	-110.05926	-565.46127	55.90219	-193.08669	-194.85295	1.754
OF <sub>2</sub>	HF/3-21G	-165.53200	-794.74176	72.76738	-272.01147	-278.23157	1.643
	HF/6-31+G**	-167.09068	-806.13400	76.82207	-273.46365	-279.63851	1.637
	BLYP/6-31+G**	-148.23148	-795.02051	71.18403	-274.67786	-279.70819	1.853
	B3PW91/6-31+G**	-152.20186	-800.28600	73.81599	-274.56710	-279.70887	1.804
	B3LYP/6-31+G**	-152.26438	-799.01586	73.17501	-274.67284	-279.71393	1.804
	B3P86/6-31+G**	-152.78948	-800.51498	73.93487	-275.11862	-279.70510	1.801
	B3P86/6-31++G(3df,3pd)	-152.58120	-803.90752	74.70458	-275.20822	-280.49930	1.804
H <sub>2</sub> C=O	HF/3-21G	-72.69562	-329.49523	31.41273	-113.22182	-114.28704	1.557
	HF/6-31+G**	-73.17106	-331.71287	31.76539	-113.87456	-114.93518	1.556
	BLYP/6-31+G**	-63.69256	-329.88960	30.87768	-114.48494	-114.91467	1.797
	B3PW91/6-31+G**	-65.68664	-330.68601	31.23627	-114.46325	-114.94863	1.743
	B3LYP/6-31+G**	-65.73326	-330.56834	31.18553	-114.51152	-114.94169	1.742
	B3P86/6-31+G**	-66.02936	-330.73158	31.25508	-114.79028	-114.95204	1.738
	B3P86/6-31++G(3df,3pd)	-65.92228	-331.96862	31.46714	-114.82792	-115.30043	1.742
HCN	HF/3-21G	-60.78654	-264.56224	24.26271	-92.35408	-92.58721	1.519
	HF/6-31+G**	-61.11092	-265.90356	24.29410	-92.88066	-93.13515	1.520
	BLYP/6-31+G**	-52.85946	-264.57364	23.59782	-93.40913	-93.16200	1.767
	B3PW91/6-31+G**	-54.58792	-265.09634	23.83237	-93.38740	-93.18497	1.711
	B3LYP/6-31+G**	-54.63558	-265.06670	23.82724	-93.43061	-93.17667	1.710
	B3P86/6-31+G**	-54.88442	-265.13491	23.84614	-93.67108	-93.18970	1.707
	B3P86/6-31++G(3df,3pd)	-54.78304	-266.23742	24.05517	-93.70003	-93.48303	1.710

Table 2. Deviations of computed results from eq. (6): % difference =  $\left[ E_{\text{mol}} - \frac{3}{7}(V_{\text{ne}} + 2V_{\text{nn}}) \right] \frac{100}{|E_{\text{mol}}|}$



Molecule	HF/3-21G	HF/6-31+G**	BLYP/ 6-31+G**	B3PW91/ 6-31+G**	B3LYP/ 6-31+G**	B3P86/ 6-31+G**	B3P86/ 6-31++G(3df,3pd)
H <sub>2</sub> O	1.90	1.65	1.08	1.13	1.09	0.86	1.14
HCN	0.25	0.27	-0.26	-0.22	-0.27	-0.51	-0.23
N <sub>2</sub>	0.51	0.45	-0.002	0.04	-0.01	-0.22	0.11
C <sub>2</sub> H <sub>2</sub>	-0.37	-0.28	-0.89	-0.84	-0.91	-1.19	-0.93
H <sub>2</sub> C=O	0.94	0.93	0.38	0.42	0.38	0.14	0.41
CO <sub>2</sub>	1.08	1.07	0.61	0.65	0.61	0.41	0.70
	0.13	0.19	-0.30	-0.29	-0.33	-0.58	-0.32
H <sub>2</sub> C=C=O	0.47	0.50	-0.01	0.03	-0.02	-0.26	0.001
N <sub>2</sub> O	0.80	0.73	0.31	0.33	0.29	0.09	0.37
FCN	1.32	1.32	0.86	0.90	0.86	0.66	0.91
	-0.46	-0.37	-1.00	-0.97	-1.03	-1.34	-1.10
OF <sub>2</sub>	2.29	2.26	1.83	1.87	1.84	1.67	1.92
average absolute deviation	0.88	0.84	0.63	0.64	0.64	0.66	0.68

Table 3. Computed values of  $E_{\text{mol}}/\sum n_i \epsilon_i$



Molecule	HF/3-21G	HF/6-31+G**	BLYP/ 6-31+G**	B3PW91/ 6-31+G**	B3LYP/ 6-31+G**	B3P86/ 6-31+G**	B3P86/ 6-31++G(3df,3pd)
H <sub>2</sub> O	1.612	1.600	1.835	1.782	1.782	1.778	1.781
HCN	1.519	1.520	1.767	1.711	1.710	1.707	1.710
N <sub>2</sub>	1.532	1.532	1.765	1.712	1.711	1.708	1.712
C <sub>2</sub> H <sub>2</sub>	1.489	1.489	1.755	1.694	1.693	1.689	1.692
H <sub>2</sub> C=O	1.557	1.556	1.797	1.743	1.742	1.738	1.742
CO <sub>2</sub>	1.566	1.565	1.810	1.742	1.742	1.738	1.743
	1.512	1.514	1.759	1.703	1.702	1.699	1.702
H <sub>2</sub> C=C=O	1.532	1.532	1.777	1.721	1.721	1.717	1.720
N <sub>2</sub> O	1.549	1.546	1.775	1.722	1.722	1.719	1.722
FCN	1.581	1.579	1.807	1.755	1.754	1.751	1.754
	1.480	1.483	1.753	1.690	1.689	1.685	1.688
OF <sub>2</sub>	1.643	1.637	1.853	1.804	1.804	1.801	1.804
average	1.548	1.546	1.788	1.732	1.731	1.728	1.731

Table 4. Computed energy quantities (in hartrees) for benzene, aniline and nitrobenzene.

Molecule	Quantity	Method	
		HF/6-31+G**	B3P86/6-31+G**
C <sub>6</sub> H <sub>6</sub>	$\sum n_i \epsilon_i$	-155.21902	-138.03834
	$V_{ne}$	-945.88064	-944.02137
	$V_{nn}$	204.58471	203.47523
	$E_{mol}$	-230.72183	-233.02088
	$\frac{3}{7}(V_{ne} + 2V_{nn})$	-230.01909	-230.17325
	% difference <sup>a</sup>	-0.30%	-1.22%
	$E_{mol}/\sum n_i \epsilon_i$	1.486	1.688
C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>	$\sum n_i \epsilon_i$	-190.97150	-170.21654
	$V_{ne}$	-1211.67191	-1209.36796
	$V_{nn}$	272.86409	271.49366
	$E_{mol}$	-285.75786	-288.52930
	$\frac{3}{7}(V_{ne} + 2V_{nn})$	-285.40446	-285.59170
	% difference <sup>a</sup>	-0.12%	-1.02%
	$E_{mol}/\sum n_i \epsilon_i$	1.496	1.695
C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>	$\sum n_i \epsilon_i$	-285.30524	-256.28196
	$V_{ne}$	-1850.07489	-1843.22742
	$V_{nn}$	416.77305	412.92240
	$E_{mol}$	-434.19709	-437.91797
	$\frac{3}{7}(V_{ne} + 2V_{nn})$	-435.65520	-436.02112
	% difference <sup>a</sup>	0.34%	-0.43%
	$E_{mol}/\sum n_i \epsilon_i$	1.522	1.709

<sup>a</sup>Defined in Table 2.



## Figure Captions

Figure 1. Relationship between  $E_{\text{mol}}/\sum n_i \epsilon_i$  and percent deviation from eq. (6), for HF/6-31+G\*\* results. The correlation coefficient is 0.9996.

Figure 2. Relationship between  $E_{\text{mol}}/\sum n_i \epsilon_i$  and percent deviation from eq. (6), for BLYP/6-31+G\*\* results. The correlation coefficient is 0.979.

Figure 3. Relationship between  $E_{\text{mol}}/\sum n_i \epsilon_i$  and percent deviation from eq. (6), for B3P86/6-311++G(3df,3pd) results. The correlation coefficient is 0.969.

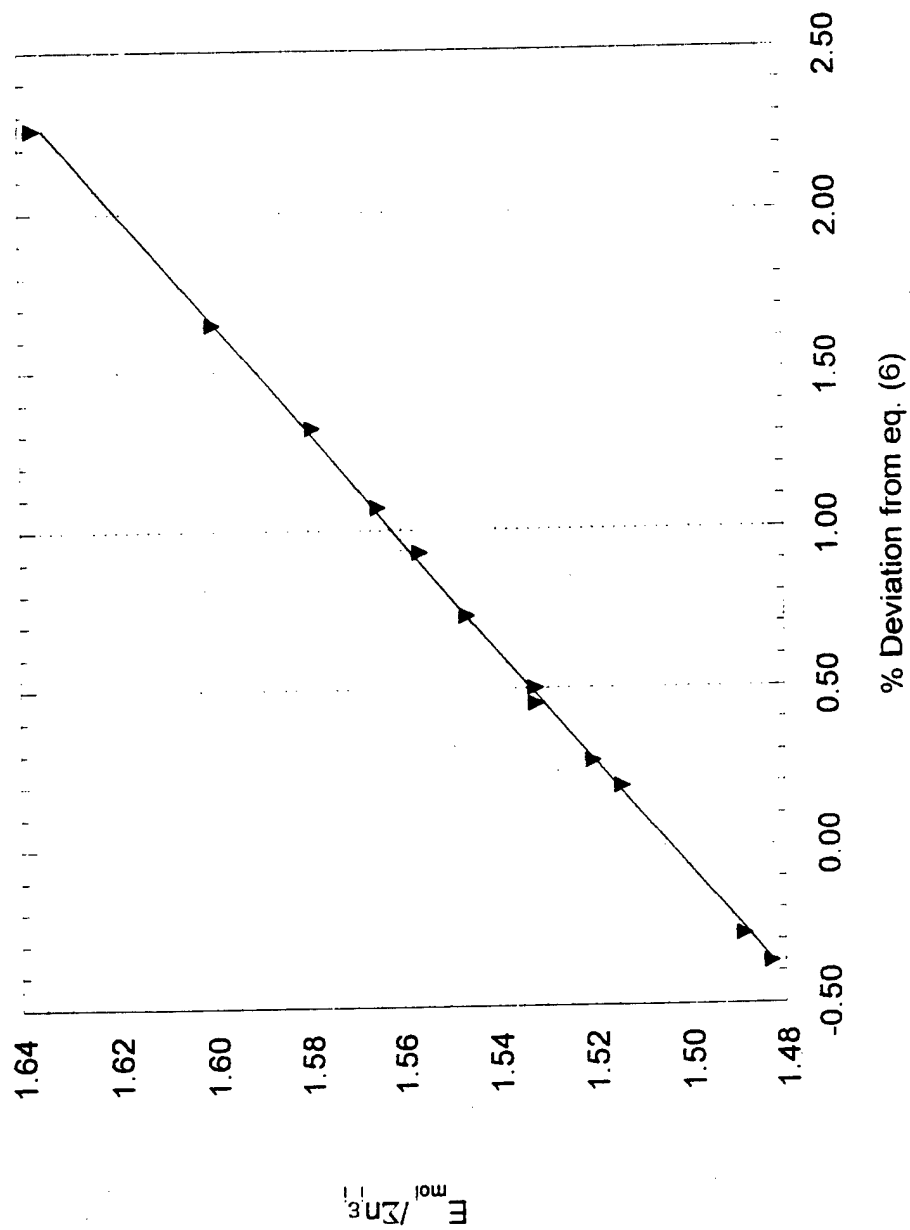


Figure 1. Relationship between  $E_{\text{mol}} / \sum n_i \epsilon_i$  and percent deviation from eq. (6), for HF/6-31+G\*\* results. The correlation coefficient is 0.9996.

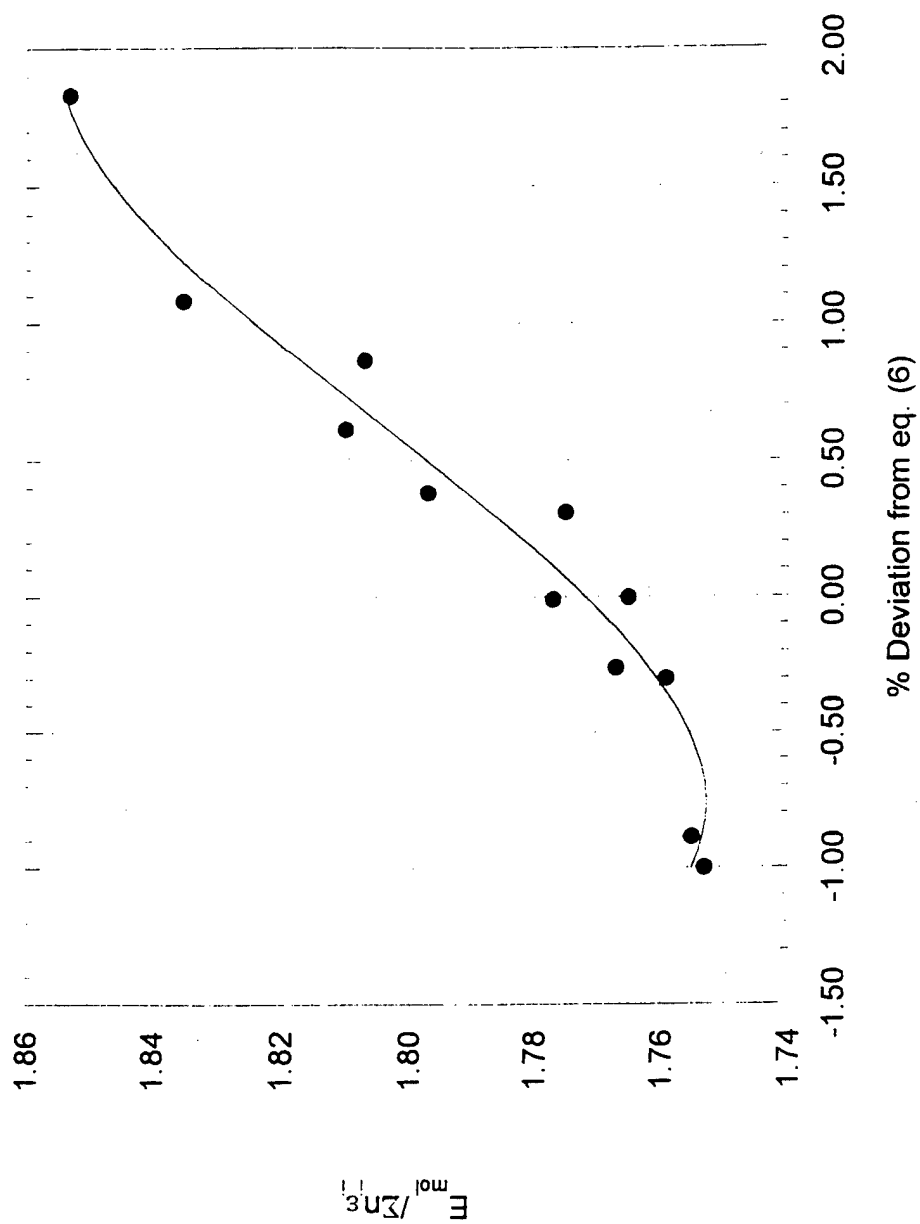


Figure 2. Relationship between  $E_{\text{mol}} / \sum n_i \epsilon_i$  and percent deviation from eq. (6), for BLYP/6-31+G\*\* results. The correlation coefficient is 0.979.

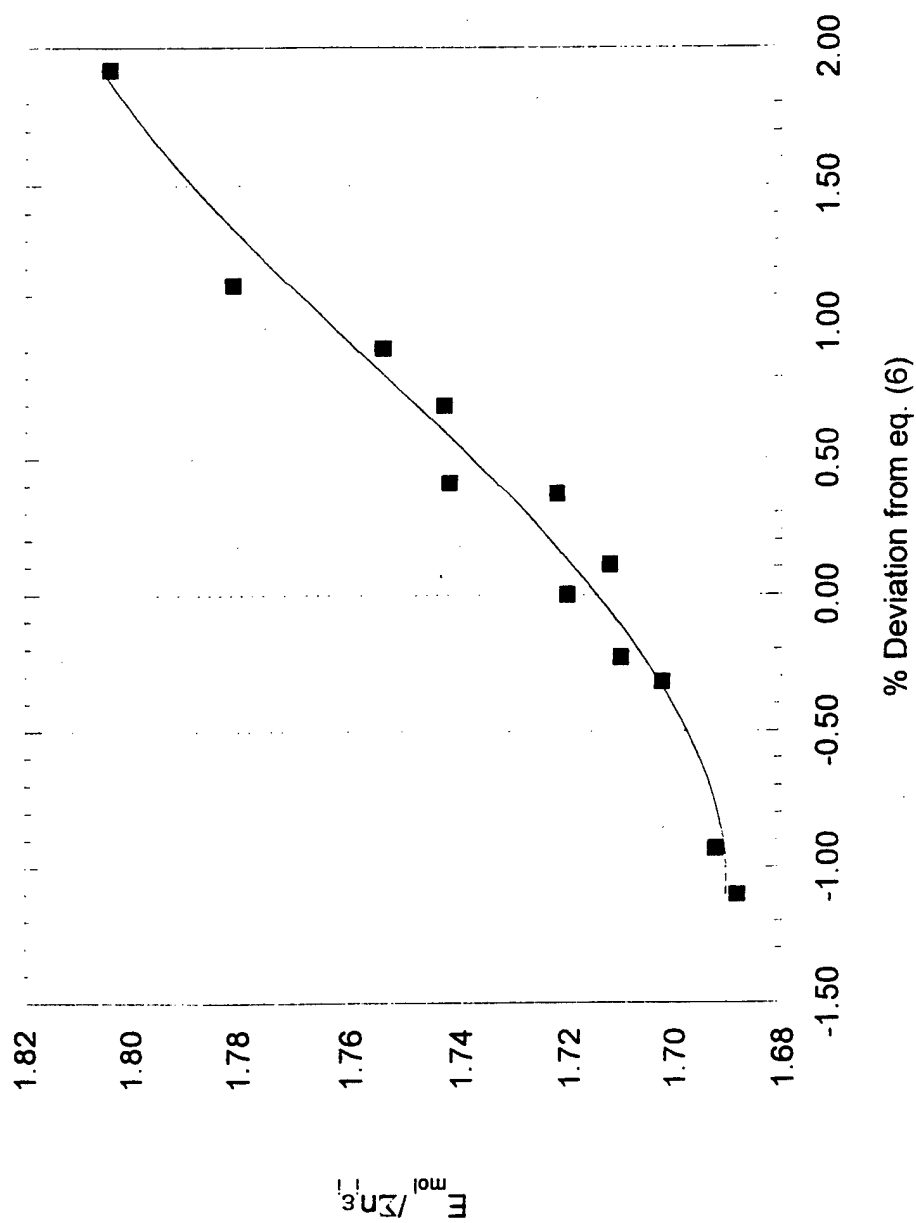


Figure 3. Relationship between  $E_{\text{mol}} / \sum n_i \epsilon_i$  and percent deviation from eq. (6), for B3P86/6-311++G(3df,3pd) results. The correlation coefficient is 0.969.